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THE SEPARATION OF COLUMBIUM
AND TANTALUM

BY

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THIS IS TO CERTIFY THAT THE THESIS PREPARED UNDER MY SUPERVISION BY

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The Separation of Columbium and Tantalum

For a great many years, in fact ever since the discovery of the elements about a century ago, chemists have been perplexed by the problem of the separation of columbium and tantalum. The resemblance of the elements and their corresponding compounds in both physical and chemical properties is so strong, that no point of divergence can be found, sharp enough to base a means of separation upon it.

A number of methods for a solution of this problem have been proposed,^{2,3} but the one found to be best applicable was that of Marignac.

The Theory of the Double Fluoride Process

Marignac^{5,6} suggested crystallization of the normal potassium fluotantalate, K_2TaF_7 , under such conditions of acidity and concentration of potassium fluoride, that the columbium should form the soluble oxyfluoride, $KCbOF_5 \cdot H_2O$. The separation is based on the fact that the two double fluorides are not isomorphous, and therefore no mixed crystals should be formed.

Obviously, this theory was accepted as a tentative solution of the difficulty. The experimental details of the problem were then studied, and the following method was adopted.

The Double Fluoride Process

The method here given is that of Wolcott Gibbs², and is very similar to the Marignac process, having preceded the latter.

The finely pulverized mineral is fused with 3 times its weight of potassium fluoride. This fusion is then digested with boiling water which has been acidified with hydrofluoric acid. Now the solution is filtered to remove quartz, potassium fluosilicate and calcium fluoride.

The next step is precipitation of any tin, tungsten or molybdenum present, by means of hydrogen sulphide. Then evaporate to dryness, add enough sulphuric acid to expel all the fluoride present. Then boil with a large amount of water, and the needles of the tantalum compound will be precipitated. These are filtered off, and upon standing, or further concentration, the thin transparent plates of the columbium salt appear.

Experimental

The residues of Norwegian Fergusonite, which had been previously treated to remove the rare earth content, were used as the source of columbium and tantalum. The mass was dried and finely pulverized. Then 25 grams of it was intimately mixed with 75 grams of well ground potassium fluoride.

To this mixture in a platinum crucible, some hydrofluoric acid was added, and the pasty mass evolved heat immediately. It was allowed to stand for a day, acid being added with vigorous stirring when the mass became hard. After removal of excess acid on the water bath, the material was dried, and then heated to fusion at $800^{\circ}\text{C}..$

The fused mass was of a whitish yellow color, but repulverization and fusion gave an almost pure white mass. The melt was then digested by boiling with water and hydrofluoric acid, and filtered to remove impurities. The hot filtrate was allowed to stand in a rubber dish, and upon cooling, a myriad of glistening, white, laminated crystals settled to the bottom. These were filtered off, and hydrogen sulphide was passed into the solution. A brown precipitate settled out and this was filtered off. Confirmatory tests showed it to be molybdenum sulphide.

Now the filtrate was neutralized with ammonia, bringing down the remaining impurities, such as rare earth, iron, etc. which I removed. The filtrate was now evaporated to dryness,

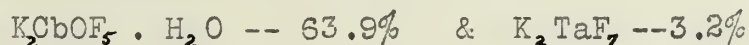
sulphuric acid added to expel the fluorine present, and then boiled with water. Upon concentration of the solution the tantalum salt appeared in needle-shaped crystals, and upon further concentration the transparent plates of potassium columbium oxyfluoride were precipitated.

Necessary weighings were made, and it remained to test the salts qualitatively. First some of the laminated salt was dissolved in water, and acidified with a drop of hydrochloric acid. To this solution, one of tannic acid in alcohol was added, and a brick-red color resulted, indicating columbium. The same test on the needle-like salt gave a sulphur yellow color, indicating tantalum.

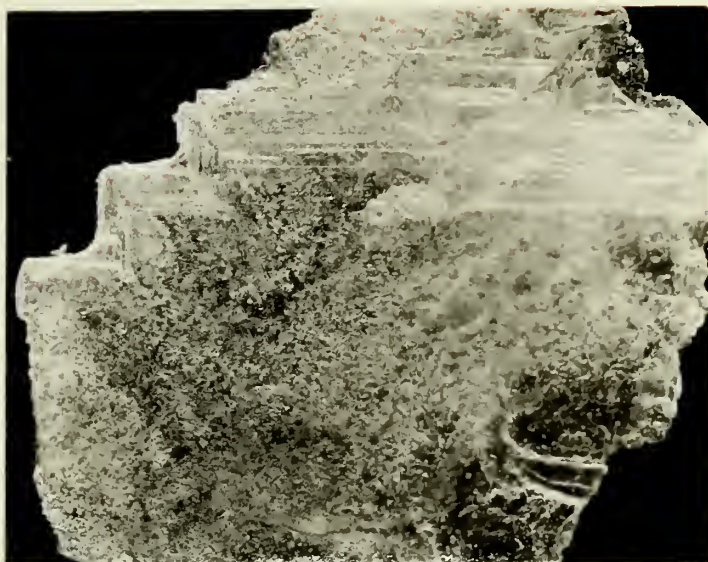
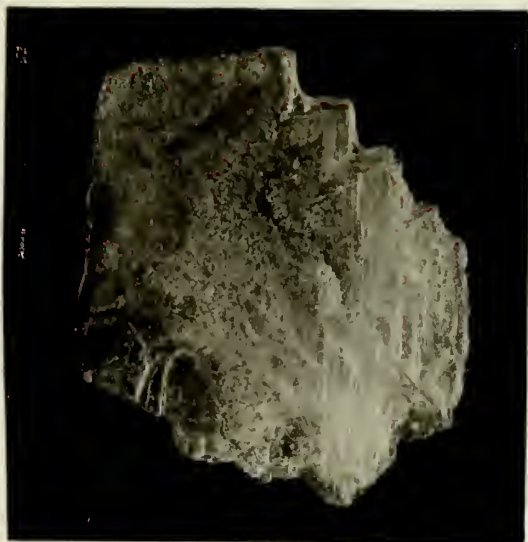
Then again, to a water solution of each salt I added an excess of potassium thiocyanate, then particles of zinc, followed by strong hydrochloric acid. At once the laminated salt solution turned brown, while the other gave no color reaction.

As a final confirmatory test, I added to a solution of each salt some potassium ferrocyanide, and heated to boiling. The solution containing the laminated crystals produced a greenish blue precipitate. This reaction confirmed the original salt as the columbium compound. The solution of the needle-like salt turned yellow, proving the presence of the tantalum salt.

After repeated separations of various samples, I got an average composition as follows:



Photographs of Crystals



Potassium Fluoxycolumbate

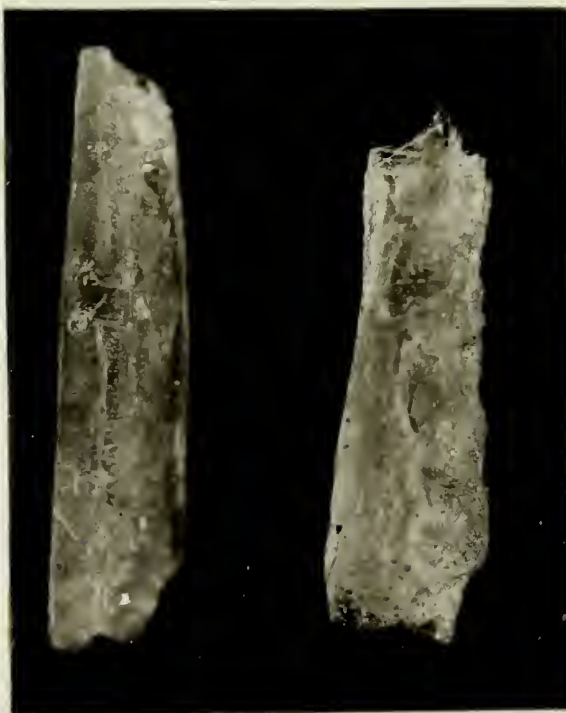
Magnif. 2 1/2 times

Magnif. 4 times



Pot. Fluoxycolumbate

Magnif. 10 times



Potassium Fluotantalate

Magnif. 10 times

Conclusion

Although the double fluoride method is a fair one, there are a number of disadvantages in it. First of all the ratio of the solubility of the columbium compound to that of the tantalum is only about 10 to 1, potassium columbium oxyfluoride being soluble in 12 parts of hot water, while potassium fluotantalate requires 120 parts. Therefore, many recrystallizations are necessary, before even an approximate separation may be attained.

Neither element can thus be obtained absolutely pure, and the limit of error is seen to be at least 10%. Furthermore, additional error may be introduced thru difficulty in maintaining the proper concentrations of hydrofluoric acid and potassium fluoride. If the acidity is too great the columbium forms a normal fluoride; if too low, the tantalum may form an oxyfluoride; in either case the basis of separation is destroyed.

If too much or too little potassium fluoride is present, double fluorides are formed, in which the ratio of potassium fluoride to columbium or tantalum pentafluoride is more or less than 2:1. Finally, the double fluoride method is extremely laborious and consumes a great deal of time, in addition to requiring the use of platinum vessels.

Theory of the Selenium Oxychloride Process.

Lenher^{8.} discovered that columbium oxide is soluble in a mixture of sulphuric acid and selenium oxychloride, while tantalum is almost insoluble in the same reagent. Evidently this ought to serve as a new and better means of attacking the old, puzzling problem. Work was begun along this theory, and the ideal experimental conditions for accomplishing the separation were found by long continued research.

The Selenium Oxychloride Method.

The mixture of columbium and tantalum oxides is separated, together with titanium when present, by the ordinary methods of procedure, from the remaining elements. Then the percentage of mixed oxides in the sample is determined. Now a weighed sample of the ignited oxides is boiled with 50 cc. of a 1:1 mixture of selenium oxychloride and sulphuric acid (conc.) in an ehrlenmeyer flask on a sand-bath for half an hour. The boiling must not be so vigorous as to give off clouds of vapor.

The contents of the flask are then allowed to cool, and then decanted with suction thru a weighed Gooch crucible. In this decantation, solid particles should not be allowed to enter the filter, because they would thus escape the necessary subsequent extraction.

The filtrate is poured into a large volume of water, and the resulting solution is heated to boiling. A voluminous white precipitate of hydrated columbium pentoxide indicates the presence of columbium in the mixture. The residue left in the flask after decantation is boiled with 20 cc. of the reagent for 15 minutes. The solution is then decanted thru the Gooch crucible, and the filtrate poured into water. This repeated extraction is continued until hydrolysis of the filtrate gives only a faint white precipitate due to traces of dissolved tantalum pentoxide.

By the above method of procedure, the stages of solution of the columbium oxide can be ascertained, and the number of extractions thus determined in order to effect complete removal. The next step in the process is to transfer the undissolved tantalum pentoxide to the crucible, by means of jet from a wash bottle. It is not necessary to wash the oxide completely, since all the decomposition products of the reagent are volatile.

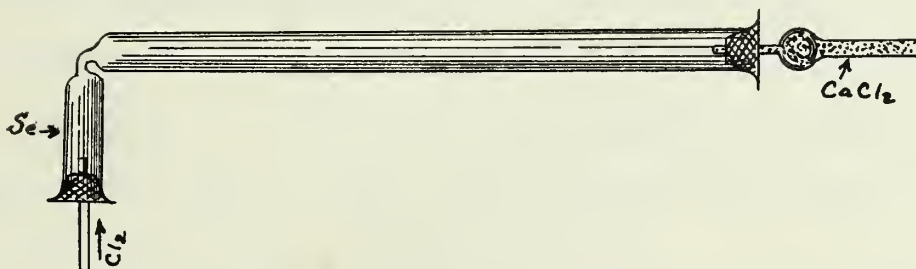
The crucible is now ignited and weighed, and the increase in weight represents the amount of tantalum pentoxide in the sample. The quantity of columbium plus titanium is determined by the difference in weights. Titanium is best determined colorimetrically in a separate sample, and its weight is deducted from that of its mixture with columbium.

Henry Baldwin Merrill⁹ applied this method to synthetic mixtures of columbium and tantalum pentoxides, and found the maximum error to be about 3 per cent. Thus, the process is seen to be not only more rapid and simple in operation than the Marignac process, but more accurate to the extent of 7 per cent.

Preparation of Selenium Oxychloride

Following the method used by Lenher,⁷ the preparation of selenium oxychloride was attempted by the interaction of selenium dioxide and tetrachloride. The addition of boiling nitric acid to powdered selenium, succeeded by the heat decomposition of the selenious acid formed, yielded a pure white product of selenium dioxide.

However, the preparation of selenium tetrachloride as advised was not very successful. Vanino¹² gives a good method in which the elements selenium and chlorine are mixed in the dry. The apparatus used is shown in the diagram.



The reaction took place violently with the generation of much heat, and the tetrachloride distilled over into the long tube.

The dioxide and tetrachloride were then mixed and dry distilled under reduced pressure. The product obtained was very much contaminated with red colloidal selenium. Repeated vacuum distillation did not purify the compound. Furthermore, extraction of the impurity with carbon disulphide was found to be impractical. The pure selenium oxychloride was therefore bought and thus used.

Experimental

Some potassium fluoxycolumbate crystals, obtained by the double fluoride process, were ignited to the pentoxide. With this compound as a basis, the selenium oxychloride method was applied in an attempt to determine increased efficiency of the latter process, as described above.

However, none of the tantalum salt was obtained thru this means..

Next a quantity of the Fergusonite residues was fused with 9 times its weight of potassium bisulphate.¹⁰ This fusion was digested with water, the insoluble part containing columbium and tantalum, and as impurities, tin, titanium, silica and possibly tungsten. The latter were removed by heating with yellow ammonium sulphide, and then treating with dilute sulphuric acid to dissolve out the iron sulphide.

Now the oxides were washed with boiling water and dried. After ignition, the color of the oxides was almost pure white.¹¹ The selenium Oxychloride was then used as a means of separation of the columbium and tantalum oxides, as described above.

By this method I found the contents to be:

Cb_2O_5 -- 45.5% and Ta_2O_5 -- 23.2%

Conclusion.

The selenium oxychloride process is very effective when used in conjunction with the opening up of an ore by a fusion in order to obtain a mixture of the tantalum and columbium oxides. The bisulphate fusion is preferable in this connection, to that of the bifluoride.

Furthermore, the oxychloride is much more rapid than the double fluoride process, since in the former the analyst is not forced to lose time in waiting for complete crystallizations to take place, as in the latter.

In short, it is likely that the selenium oxychloride may replace the old, relied-upon double fluoride process, in the near future, notwithstanding that the applicability of the former method is rather limited.

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